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Original Article

Interaction between UN and $CdCl_2$ in molten LiCl-KCl eutectic. I. Experiment at 773 K

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ABSTRACT

The interaction between UN and $CdCl_2$ in the LiCl-KCl molten eutectic was studied at 773 K.

The reaction was controlled by sampling the melt, as well as by analysis of the resulting precipitate. The process was shown to proceed according to several parallel reactions. The summary reaction was determined to have two stages: a fast one and a slow one. The 19–53% UN → UCl_3 conversion was obtained for the molar ratio of $CdCl_2$/UN = 1.22–14.9. The rest of UN converts into the precipitate of complex composition (UNCl + U_2N_3 + U_4N_7 + UN_2). The increase in the $CdCl_2$/UN molar ratio from 1.22 to 14.9 resulted in the decrease in duration of the first "fast" stage of the process from 18 h to 1 h.

1. Introduction

Uranium resources limitations and toughening of ecological requirements are driving forces of development of new approaches in nuclear fuel cycle chemistry. The ultimate goal is to create a closed fuel cycle with reuse of uranium and plutonium and recycling of long-lived actinides. Spent nuclear fuel (SNF) being a heavy burden on atomic power engineering, today is recycled using hydrometallurgical technologies. Water chemistry requires prolonged cooling of the fuel prior to reprocessing, that causes a large amount of liquid radioactive wastes. A need for a new approach to reprocessing of spent nuclear fuel has reached a crisis point due to the development of the fast-neutron reactor concept and due to the introduction of nitride nuclear fuel to the fuel cycle [1–5]. Economic feasibility and safety are crucial features of modern technologies. Pyroprocessing in molten salts is supposed to be both more economical and safe method for the SNF reprocessing. Molten salts are highly resistant to radiation damage; therefore, the SNF cooling period could be greatly shortened and a scale of repositories could be considerably decreased. Moreover, the pyrochemical technology can provide the lowest possible volume of final disposals. This technology also prevents the spread of radioactive materials, even in the event of severe accidents. As opposed to devices with aqueous solutions or organic liquids, molten salts solidify quickly and the accident will be localized in a small area even though cell body is damaged. All above-mentioned positive features make the pyrochemical technologies prospective for reprocessing of nitride SNF.

One of the initial stages of pyrochemical reprocessing of nitride SNF is suggested to be the SNF dissolution in the molten LiCl-KCl eutectic. Having high electron conductivity, nitrides of uranium, plutonium and rare earth metals can be electrochemically dissolved in molten salts. Several studies were performed with different components of nitride SNF to prove the feasibility of the pyrochemical method application. The actinides behavior at the nitrides electrolysis in the LiCl-KCl eutectic melts was studied to determine the UN, NpN, PuN, AmN, (U, Pu)N, (U, Pu, Np, Am)N and burnup-simulated uranium nitride fuels behavior [6–13]. The anode dissolution of UN was reported to be accompanied by a generation of such insoluble compounds as U_2N_3 and UNCl [7,8,14].

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These side products may become a serious problem for the technology. For example, the UN → UCl_3 conversion in the experiment reported in Ref. [8] was about 24%. The electrolysis at the constant anode potential of 0.65 - 0.60 V vs Ag/AgCl was found [15] to result in the 90% dissolution of UN in the LiCl-KCl eutectic at 773 K. Shirai *et al* reported that plutonium nitride dissolved with the efficiency up to 90% [11]. The lowest efficiency of 20–28% was achieved at the dissolution of AmN [12]. Such low current efficiencies for AmN may occur due to the current circulation caused by the Am^{3+}/Am^{2+} reaction, which takes place at the electrodes. Previous investigations also demonstrated that the electrochemical process of nitrides dissolution might be very slow [8,10].

Chemical dissolution in a chloride melt with different oxidizing agents is an alternative way for pyrochemical reprocessing of SNF. The use of gaseous agents (Cl_2, HCl, CCl_4) for this means brings additional technological challenges. It is much more convenient to use "soft" chlorinating agents, such as $CdCl_2$ or $PbCl_2$. The following reactions are supposed to occur during this process:

$$UN + 1.5CdCl_2 = UCl_3 + 1.5Cd + 0.5N_2\uparrow\ \Delta G = -58.7\ \text{kJ/mol at } 773\ \text{K} \quad (1)$$

$$PuN + 1.5CdCl_2 = PuCl_3 + 1.5Cd + 0.5N_2\uparrow\ \Delta G = -234\ \text{kJ/mol at } 773\ \text{K} \quad (2)$$

Cadmium chloride was used as a chlorinating agent for nitride SNF to dissolve ZrN, NdN, DyN, UN, U_2N_3 ($UN_{1.6}$), UNCl, PuN, (Pu, Zr)N and PuN + TiN at lab scale experiments [16–21]. All experiments were performed using powder samples. Even if solid tablets were obtained after the synthesis or sintering, they were ground to powder for experiments on the dissolution of PuN, PuN + TiN [14]. In research [17] the samples of NdN, DyN and ZrN were kept in $(LiCl\text{-}KCl)_{eut.} + CdCl_2$ at a gradual temperature rise up to 873 K. The volume of nitrogen formed in the reaction was evaluated. The NdN → $NdCl_3$ dissolution yield was 88–93%, for DyN → $DyCl_3$ it was 97–99%, and for ZrN it was 0.3%. The increase in $CdCl_2$ content was found to increase the dissolution. Hayashi *et al* [18] reported that the samples of UN, U_2N_3 ($UN_{1.6}$) UNCl and ZrN of 0.2–0.5 g were heated stepwise in molten $(LiCl\text{-}KCl)_{eut.} + CdCl_2$ (approximately 10 g in total) up to the temperatures of 993–1073 K. According to the volume of nitrogen formed the calculated conversion of UN → UCl_3 was 83–100%, for U_2N_3 → UCl_3 it was 86%, for UNCl → UCl_3 it was 83%, and the dissolution of ZrN was about 3%. The conversion degree was reported to be independent of the $CdCl_2$ concentration. Researchers [16] exposed the PuN, (Pu, Zr)N and PuN + TiN samples in amount of 100–120 mg in the same melt during 12 h at the constant temperatures of 723, 773 or 823 K. The molten salt samples were taken for analysis every 1–2 h. Plutonium dissolved in the melt completely both from PuN and from solid solutions with ZrN or TiN at the temperatures of 773 and 823 K. The dissolution of ZrN was 0.12–0.18%, and TiN remained undissolved. The temperature had a strong influence on the dissolution rate of PuN and the efficiency of the PuN → $PuCl_3$ reaction. The yield achieved was 63.8% at the temperature of 723 K.

Accepting the SNF dissolution in the LiCl-KCl melt with $CdCl_2$ additions as a basic process of the pyroprocessing allows separating noble metals and Zr from chlorides of actinides, lanthanides, alkali and alkaline-earth elements. It gives us opportunity to detach an essential portion of radioactivity at the first stage of the process. Real nitride SNF is a multicomponent system. But UN, the content of which amounts 80–90%, is the main component. By now, the UN chlorination process by $CdCl_2$ requires a further study. Paper [18] is practically the only available data on the process.

The aim of the present work is the experimental study of the chemical interaction between uranium nitride and cadmium chloride in the molten LiCl-KCl eutectic at the temperature of 773 K. Compared with [18], we used significantly larger UN tablets and melt quantities. This allowed us to study the composition of deposits in more detail. In addition, we controlled the composition of the melt during the reaction by sampling and recorded the potential of the medium. The aforementioned allowed us to propose the assumption on potential-determining particles.

The temperature 773 K was chosen as a compromise between two opposite tendencies:

1. Lower temperatures reduce the energy consumption, construction material corrosion, and evaporation of salts, etc. The LiCl-KCl eutectic melting point, $t_m = 625$ K is the low limit of the temperature range for our medium [22]. According to reaction (1) metallic cadmium is formed during the process. Its vapor pressures are 4.43 mm Hg (723 K); 13.5 (773 K); 35.7 (823 K) and 84.3 (873 K) [23]. To prevent the evaporation of large amount of cadmium the melt temperature should be minimal.
2. During the process of the real SNF dissolution in LiCl-KCl the bulk melt accumulates UCl_3, $PuCl_3$, $LnCl_3$ (Ln - lanthanides) and other chlorides. This fact leads to a significant liquidus temperature rise [24–26]. The usual practice to avoid the unintentional solidification of the melt is overheating for at least 50° above the liquidus temperature.

Taking into consideration the above-mentioned issues our study was performed at the temperature of 773 K.

2. Experimental

2.1. Chemicals

The mixtures under investigation were prepared from individual salts LiCl (reagent grade, anhydrous, 99.2 wt %), KCl (reagent grade, 99.8 wt %) and $CdCl_2 \cdot 2H_2O$ (reagent grade, 99.7% wt. %).

To get rid of residual moisture the initial LiCl salt was heated in a quartz container under vacuum according to the following regimes:

- 0.3°/min in the temperature range from 353 to 423 K;
- 1.4–1.5°/min in the temperature range from 423 to 823 K;

The heating rate at the temperatures above 823 K was not controlled. Then the salt was melted. The criterion for the further temperature rise was a decrease in the residual pressure of the system below 1 mm Hg. Initial KCl was slowly heated to the melting point and exposed for 30–60 min in air atmosphere to burn up the traces of organics. Prepared LiCl and KCl were thoroughly purified by zone refining, which is a widely used technique for obtaining high purity salt reagents. The rate of the nickel boat with the salt mixture during the refining process was about 3 cm/h. Pure argon was flown through the experimental quartz tube in the opposite to the container movement direction. A contaminated third part of the salt ingot was removed after the refinement and was not used in further work. $CdCl_2$ salt was carefully dried under vacuum, was melted and was exposed for an hour in chlorine gas atmosphere and afterwards it was sublimated under evacuation. UN was synthesized from metallic uranium using the hydration-dehydration-nitridation method. Tablets of 6.0 ± 0.2 mm diameter, 5.3 ± 0.1 mm height and 12 ± 0.7 g/cm^3 density were used in the experiments. The composition of the tablets according to the analysis was: U - 94.1 wt%; N - 5.2 wt %; O - 0.18 wt%; C - 0.43 wt%; Fe - 0.35 wt%, Mo - 0.13 wt%; the total impurities (elements other than U and N) content was 1.03 ± 0.30 wt%. One unbroken single-part tablet was used in each experiment. An X-ray diffraction analysis of the original UN sample revealed no peaks of impurities.

2.2. Experimental cell

A scheme of the experimental set up is given in Fig. 1. The cell consisted of a quartz tube with an internal diameter of Ø 62 and a height of 330–400 mm. It contained a BeO crucible of ~50 cm^3 volume. A thoroughly weighted beforehand salt mixture of $(LiCl\text{-}KCl)_{eut.} + CdCl_2$ was put in to the crucible. A nonhermetic fluoroplastic stopper of the quartz test tube had holes for a Pt/PtRh thermocouple, for sampling tubes and a holder for a container with UN. The stopper and heat protecting shields provided rigidness of the construction and prevented the salt and cadmium vapor release into the glove box. To monitor the dissolution reaction, the potential of the molybdenum container with UN inside was recorded during some experiments. The potential was measured with respect to a reference electrode (RE), which was a silver wire immersed into the LiCl-KCl + 5.00 wt% AgCl melt kept in a 7 mm diameter BeO tube. The potential of the reference electrode was calibrated against the chlorine reference electrode. The potential was −1.24 V *vs.* Cl_2/Cl^- at 773 K.

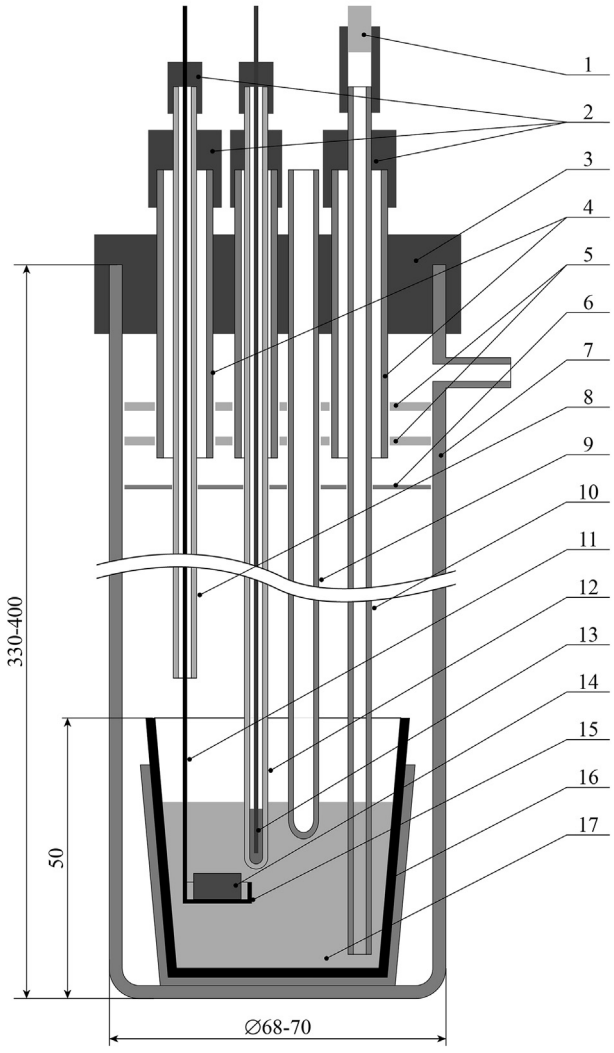

Fig. 1. Experimental set up: 1 - glass plug, 2 - vacuum rubber plugs, 3 - fluoroplastic cover, 4 - quartz tubes, 5 - fluoroplastic heat-reflecting screens, 6 - molybdenum heat-reflecting screen, 7 - quartz test-tube, 8 - alundum tube, 9 - quartz cover for the thermocouple, 10 - quartz capillary for sampling, 11 - sample holder; 12 - Ag/AgCl reference electrode, 13 - silver wire, 14 - UN tablet, 15 - Mo container for UN, 16 - BeO crucible in the nickel protective shell, 17 - melt.

2.3. Experimental procedure

All preparatory work, which included weighing, loading the cell, the experiment procedure and sampling, was carried out in a glove box with dry argon atmosphere. The amount of gas impurities was controlled (H_2O < 1 ppm; O_2 < 3 ppm). All ceramic parts of the experimental setup were heated to the temperature ~1025 K prior to use. The quartz test tube with the BeO crucible and the salt mixture loaded were immersed into the furnace, were heated to 773 K and were exposed for at least 10 h to achieve the melt homogenization. Usually they were left overnight. During this period, the container with UN was in the upper, cold zone of the test tube.

A sample of the initial salt was taken before every experiment. Then the UN container was immersed into the melt. Samples (50–300 mg) were taken periodically with a quartz capillary. Before sampling the melt was stirred with capillary. Usually the samples are easily removed from the capillary. They were then dissolved in acidified (HCl) water and analyzed for Li, K, Mo, Be, Cd, and U content. After every experiment the samples of the melt, all deposits and sublimates were carefully collected and analyzed. The elemental analysis was carried out by the emission spectral method with inductively coupled plasma using an Optima 4300 DV PerkinElmer instrument (ICP). The phase analysis was performed with a Rigaku D/MAX-2200VL/PC device. All samples were analyzed in the Shared Access Centre “Composition of Compounds” of the Institute of High Temperature Electrochemistry. In some experiments the potential of container with UN was controlled. The potential record allowed assuming whether the dissolution proceeds, the process is finished or it is obstructed.

3. Results

The results of two typical experiments are presented in Figs. 2–12. The generalized experimental data are given in Figs. 12 and 13. Fig. 2 presents the results of the experiment with a relatively low molar ratio of $CdCl_2$/UN equal to 4.42 (Exp. 1.4). As chemical reaction (1) proceeds, the cadmium chloride concentration decreases and reaches almost constant values approximately after 10 h of the experiment. The uranium chloride concentration increases and reaches the plateau correspondingly. Further changes in the concentrations become very slow. According to equation (1) the formation of 1 mol of UCl_3 requires 1.5 mol of $CdCl_2$. A dashed line in Fig. 2 is referred to the stoichiometry of the $CdCl_2$ consumption. In fact, the amount of cadmium chloride consumed is 1.6 times higher than it is necessary for the UCl_3 formation.

The potential dependence of the Mo container with UN inside was recorded during this experiment. The results are given in Fig. 3. For comparison the equilibrium potential of Cd calculated from the chemical analysis data is provided in Fig. 3 as a dashed line. At the start of the dissolution when the UN sample is immersed into the melt the recorded potential is equal to the cadmium potential. Further dissolution leads to the positive change in the potential of about 0.15V during the experiment.

The color of initial salt sample, prior to the immersion of the container with UN into the melt, was white. Further samples were purple. The longer was the experiment time, the richer the color became. The last sample and the melt ingot after cooling had the same purple color. The pictures of the crucible and the melt after the experiment are presented in Fig. 4. The salt had pink-purple color that is typical for UCl_3. Metallic cadmium droplets were found on the bottom of the crucible (Fig. 4b and c). The bottom part of the salt was dark, almost black (Fig. 4b and d). After the experiment the deposit of the same color was also discovered on the

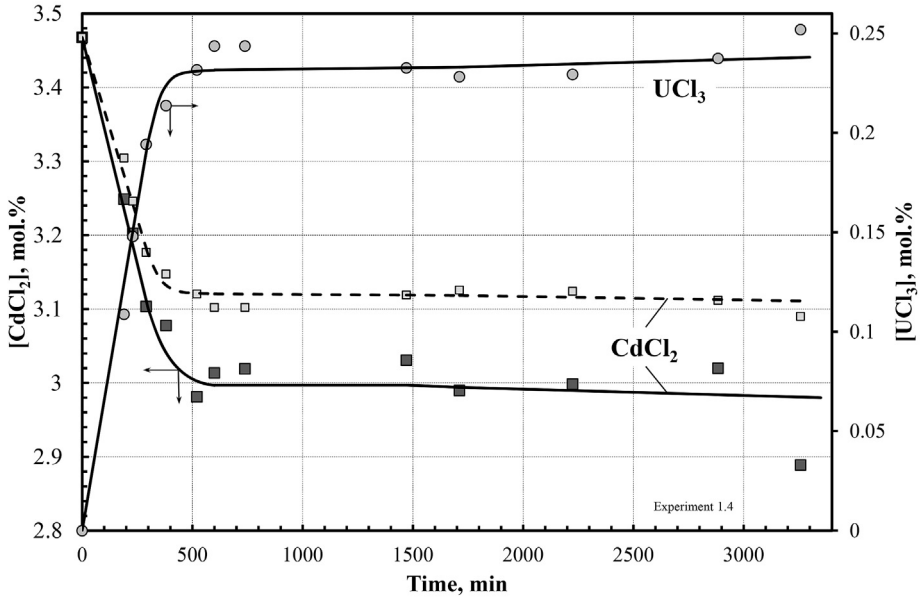

Fig. 2. $CdCl_2$ and UCl_3 concentration time dependences in Exp. 1.4. For $CdCl_2$ a solid line denotes the experimental data, a dotted line denotes the theoretical curve. Initial masses: m(UN) = 1.87g; m($CdCl_2$) = 6.0 g; m(LiCl-KCl) = 50.7 g $[CdCl_2]_{init.}$ = 10.6 wt% = 3.47 mol.%. Initial molar ratio $CdCl_2$/UN = 4.42.

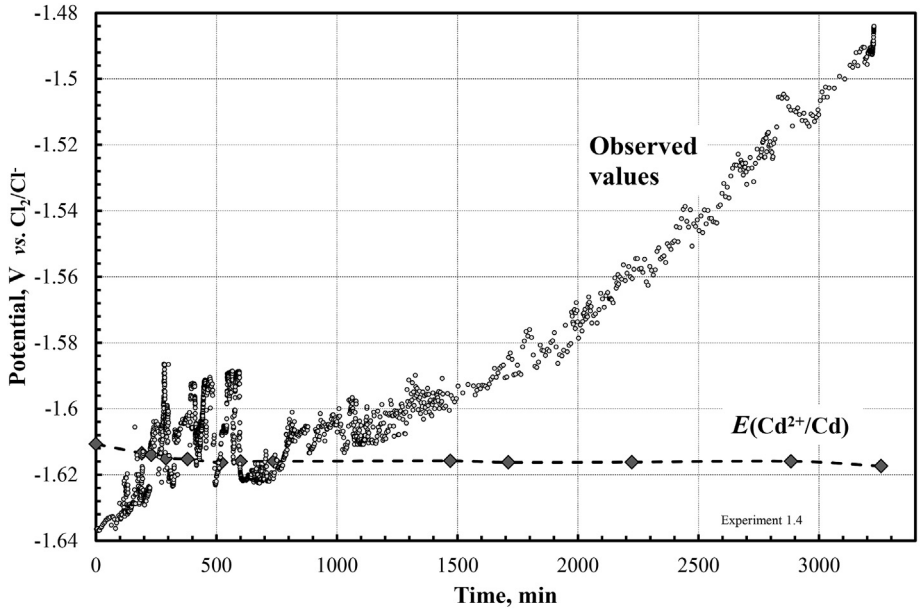

Fig. 3. Time dependence of the potential of molybdenum container with UN in Exp. 1.4. Sharp peaks correspond to sampling. A dashed line denotes the calculated equilibrium potential of cadmium in the melt.

bottom of the Mo container that contained the UN tablet. The precipitates were mechanically separated from the frozen melt and subjected to the X-ray phase analysis. The results of the analysis are given in Figs. 5 and 6. The deposits analyzed had a complex composition. First X-ray diffraction pattern showed the presence of UNCl, UN_2, K_4CdCl_6, LiCl, KCl. It is important to notice that initial UN was not detected. The deposit from the bottom of the crucible contained the U_2N_3, U_4N_7, UN_2, UO_2, LiCl, KCl and K_4CdCl_6 phases. The uranium mononitride also was not discovered in the sample. The X-ray diffraction patterns also had some small non-assigned peaks.

The sublimates observed at the top of the experimental container were thoroughly collected and analyzed after experiment. They contained about 91 wt % of metallic cadmium. The rest of the sample consisted of $CdCl_2$, LiCl and KCl. The X-ray diffraction pattern of the sublimates is shown in Fig. 7. The phases of metallic Cd and the phase of LiCl were detected.

The results of the experiment with a relatively high molar ratio $CdCl_2$/UN = 14.9 (Exp. 1.6) are presented in Fig. 8. In experiment 1.6 the mass of the uranium nitride tablet was 1.83 g. As for previous experiments, according to chemical reaction (1), the cadmium chloride concentration decreased with time and the UCl_3 content increased. Fig. 9 demonstrates the initial stage (≈6 of 50 h) of the concentration-time dependence. It is seen that at such high $CdCl_2$/

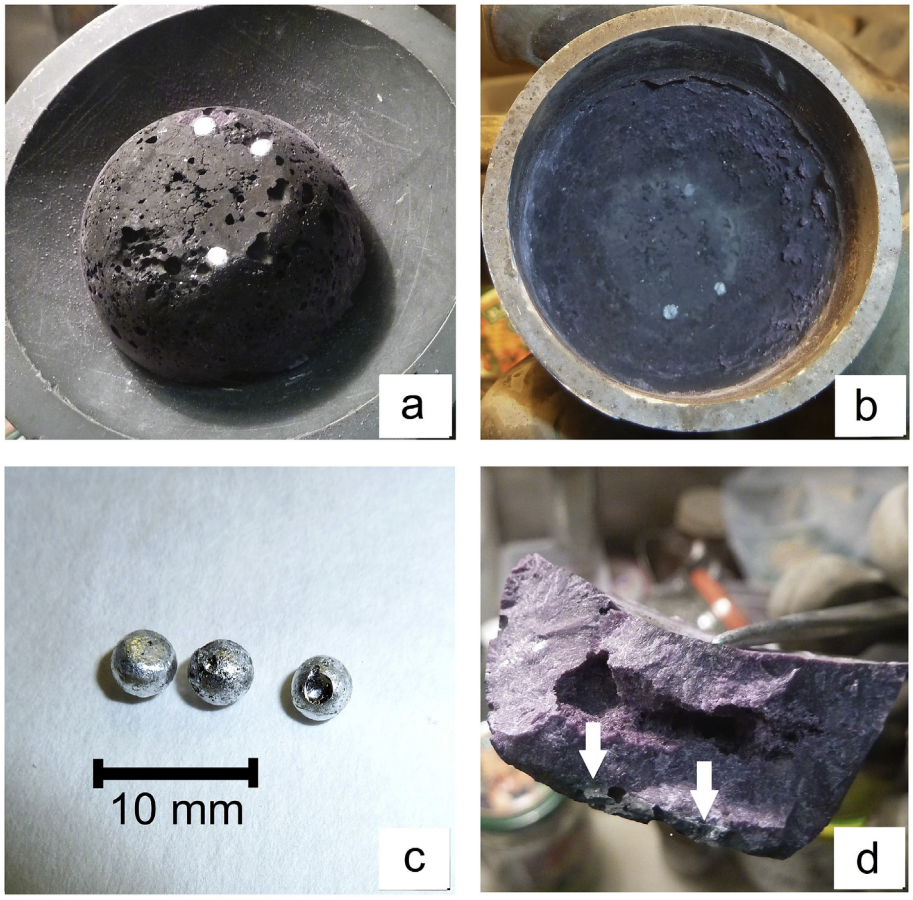

Fig. 4. (a) - Bottom part of the frozen salt in Exp. 1.4. White spots are metal cadmium balls; (b) - bottom part of the BeO crucible after the experiment (without salt). White spots are traces of cadmium; (c) - washed cadmium balls; (d) - cross section of the salt ingot. A dark precipitate is in the lower part.

UN molar ratio, the interaction between UN and $CdCl_2$ is supposed to terminate approximately in 1 h after the UN immersion into the melt (Fig. 9). However, the slow interaction continued even after 50 h of our experiment, as it can be seen in Fig. 8. Generally, the higher is the $CdCl_2$/UN molar ratio the faster is the UN + $CdCl_2$ interaction (compare Figs. 2 and 8).

The changes in the potential of the container with UN during experiment 1.6 are presented in Fig. 10. After the immersion of the uranium nitride into the melt the value of the container potential was close to the cadmium equilibrium potential. Further shift to more positive values was observed. For comparison, the dependence of the cadmium equilibrium potential calculated for $CdCl_2$ concentrations taken from the chemical analysis data is presented as a dash line in Fig. 10.

The color of initial melt sample was white. The sample taken 30 min after the UN container immersion into the molten salt was dark purple. All subsequent samples were black. After the experiment deposits from the bottom of the UN container and the crucible as far as all salt samples and sublimates were analyzed. The X-ray diffraction patterns of both deposits did not differ from those presented in Figs. 5 and 6. The samples contained mainly the UNCl, U_2N_3, U_4N_7, UN_2, LiCl, KCl, K_4CdCl_6 phases. Some weak peaks were not assigned. The mass of sublimations amounted to ~0.58 g. They consisted of 87 wt% of Cd; 5.9% of $CdCl_2$. The remaining part was identified as LiCl and KCl. The X-ray diffraction pattern of the sample is presented in Fig. 11. The phases of Cd and $CdCl_2$ were detected.

We also performed experiments on the analysis of the gaseous phase. The cell space was closed during this experiment. As chemical reaction (1) proceeded the content of nitrogen in the experimental cell rose. After 10 h of the process the basic reaction finished. Nevertheless, a slight increase in the nitrogen concentration indicated that a slow interaction continued. The analysis of the salts and deposits did not differ significantly from the previous results. The metallic cadmium content in the sublimates was ≈77 wt %.

Fig. 12 demonstrates the dependence of the UN → UCl_3 conversion degree on the $CdCl_2$/UN molar ratio at 773 K. The conversion was calculated for the highest concentration of uranium in the melt achieved at each experiment. The higher $CdCl_2$/UN molar ratio values result in the higher conversion degree. At $CdCl_2$/UN = 14.9 the conversion achieves 53%. However, 100% UN → UCl_3 conversion, apparently, cannot be achieved at 773 K. The duration of the fast stage of reaction depending on the molar $CdCl_2$/UN ratio at 773 K is given in Fig. 13. The higher value of the $CdCl_2$/UN ratio leads to the faster reaction rate. The increase in the ratio from 1.22 to 14.9 results in the decrease in the first stage duration from 18 to 1 h.

4. Discussion

In all experiments, the time dependences of the $CdCl_2$ and UCl_3 concentrations in the studied LiCl-KCl eutectic melt are substantially similar to the dependences shown in Figs. 2, 8 and 9. In these Figures the scattering of experimental points exceeds the chemical analysis technique error (±4%), because the salt samples were taken from the nonequilibrium melt. During the process of interaction

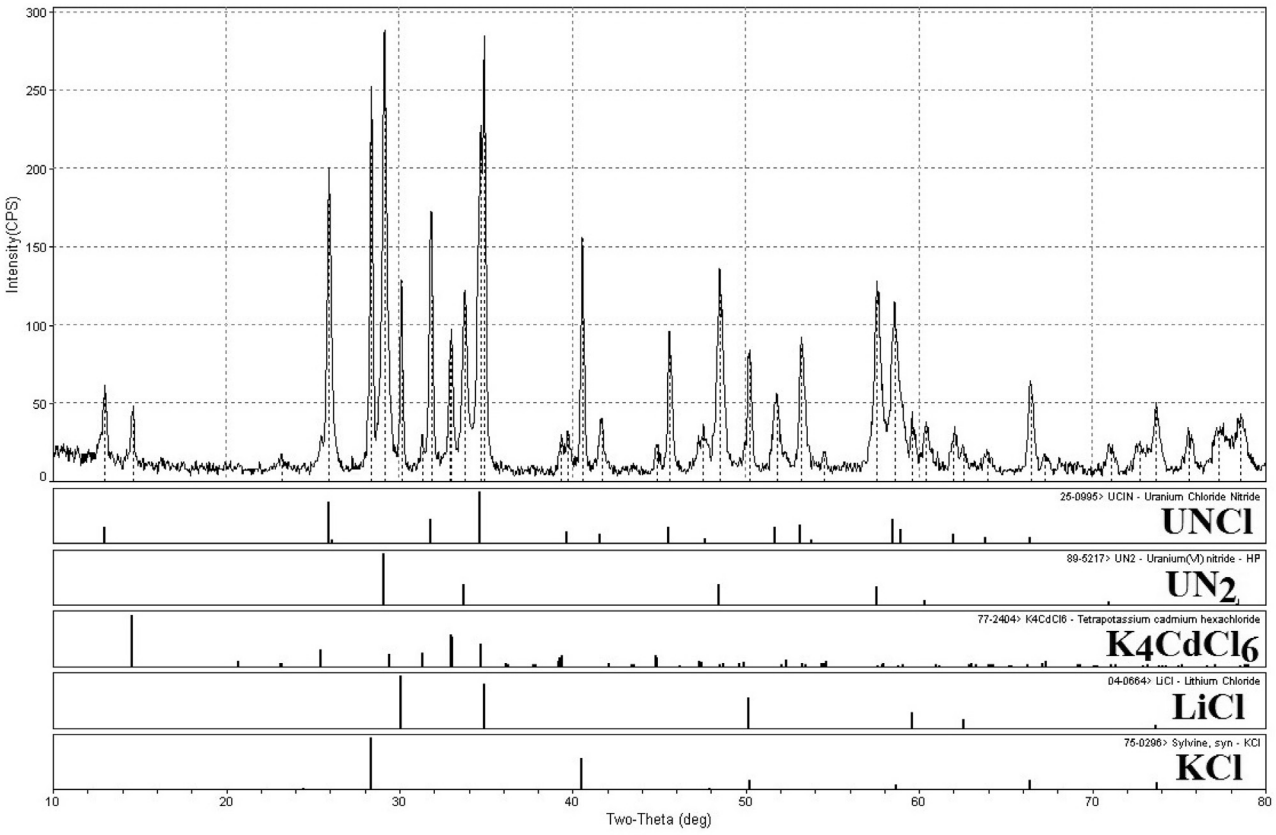

Fig. 5. X-ray diffraction pattern of the black deposit from the bottom of Mo container in Exp. 1.4.

between UN and $CdCl_2$ the bubbles of nitrogen form at the surface of UN and metallic cadmium evaporates from the melt. That is why during the experiment there is a somewhat non-equilibrium distribution of the elements in the crucible. As follows from Fig. 12, the higher $CdCl_2$/UN ratio results in the higher UN → UCl_3 conversion. It is difficult to estimate the maximum conversion that can be achieved at 773 K. According to our data, it is obvious that a large excess of $CdCl_2$ is required for high conversion. The $(LiCl\text{-}KCl)_{eut.}$ - $CdCl_2$ system at this temperature has a natural limit in the $CdCl_2$ concentration of 72–74 mol.% (~90 wt%), when the liquidus temperature exceeds 773 K [27]. The melting point of cadmium chloride is 841 K [28]. From the practical point of view, the use of such excess of chlorinating agent is unacceptable.

Two stages of reaction are clearly observed from Figs. 2, 8 and 9. The first stage of the reaction is relatively fast and after it the concentrations of $CdCl_2$ and UCl_3 reach the almost horizontal plateaus. In the second stage, the reaction, although slowly, continues. At the low value of the $CdCl_2$/UN molar ratio this tendency is hardly noticeable (Fig. 2), but at the higher $CdCl_2$ content in the melt the second stage of the UN + $CdCl_2$ interaction becomes more visible (Figs. 8 and 9).

From the abovesaid, it follows that the UN + $CdCl_2$ interaction proceeds through several parallel reactions and reaction (1) is only one of them. Because in all experiments the black deposits containing UNCl, U_2N_3, U_4N_7 and UN_2 were found at the bottom of the crucible, the following probable reactions may be suggested:

$$UN + 0.5CdCl_2 = UNCl + 0.5Cd \quad (3)$$

$$UN + 0.5CdCl_2 = 0.333U_2N_3 + 0.5Cd + 0.333UCl_3 \quad (4)$$

$$UN + 0.643CdCl_2 = 0.143U_4N_7 + 0.643Cd + 0.429UCl_3 \quad (5)$$

$$UN + 0.75CdCl_2 = 0.5UN_2 + 0.75Cd + 0.5UCl_3 \quad (6)$$

Since at the end of the experiments the initial UN was never detected, therefore, it was completely consumed in the first stage of the reaction. Reactions (1), (4), (5), (6) are accompanied by the consumption of cadmium chloride and formation of uranium trichloride in the proportion of 1:1.5. The experimental curves of the $CdCl_2$ concentration (see solid lines in Figs. 2, 8, 9) correspond to the sum of all reactions listed above. Apparently the difference between experimental and theoretical $CdCl_2$ (dash lines in Figs. 2, 8, 9) concentrations is explained by reaction (3) of UNCl formation, at which $CdCl_2$ is consumed without the UCl_3 formation. In this way, the amount of chlorinating agent spent on the UNCl formation can be estimated. The theoretical value is the concentration of $CdCl_2$ that is nessasary for generation of UCl_3, which was experimentally obtained according to reaction (1). In experiment 1.4 (Fig. 2) the consumption of $CdCl_2$ was 1.6 times higher than the amount needed for reaction (1). In experiment 1.6 (Figs 8, 9) this excess was approximately 1.35. Generally, the consumption of $CdCl_2$ during the experiments is 1.3–1.8 times higher than theoretical one. There is a tendency that the values of $[CdCl_2]_{real}/[CdCl_2]_{theory}$ ratio decrease as the value of the $CdCl_2$/UN molar ratio increases, despite the considerable experimental data scattering.

The dissolution of UNCl and/or other nitrides at the excess of $CdCl_2$ is likely to be the second “slow” stage of the process. These are possible reactions:

$$UNCl + CdCl_2 = UCl_3 + Cd + 0.5N_2 \quad (7)$$

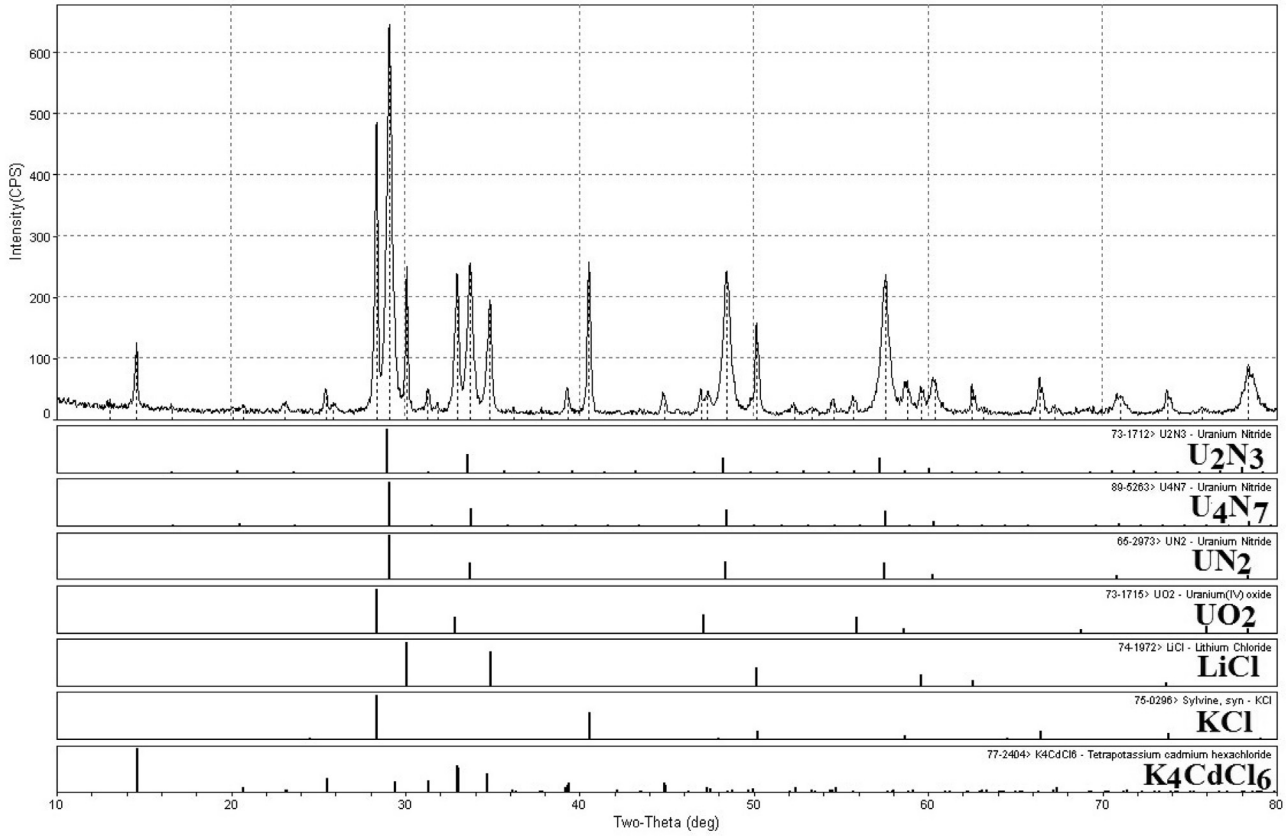

Fig. 6. X-ray diffraction pattern of the black deposit from the bottom crucible in Exp. 1.4.

$$U_2N_3 + 3CdCl_2 = 2UCl_3 + 3Cd + 1.5N_2 \quad (8)$$

The higher content of $CdCl_2$ increased the reactions rates, compare Fig.2 and Figs. 8 and 9.

Figs. 3 and 10 illustrate the graphs of the change in the potential of the melt during the experiments. The potential was measured between the molybdenum container with UN (indifferent electrode) and the Ag/AgCl reference electrode. Sharp fluctuations in the potential curves correspond to the sampling time. In all experiments, the UN tablet was initially inside the container (see Fig. 1). At the end of the experiments, in the Mo container there were UNCl, U_2N_3, U_4N_7, UN_2 nitrides, which did not contain any UN traces. Theoretically, we may suggest that there are three potential-determining couples in our melt: Cd^{2+}/Cd; U^{3+}/UN and U^{4+}/U^{3+}. Cadmium metallic generation starts immediately after the UN immersion into the melt. As a result, the Cd^{2+}/Cd potential-determining couple forms. Since the concentration of $CdCl_2$ in the melt is known, we calculated the equilibrium potential of cadmium in the melt. It is presented as a dashed line in Figs. 3 and 10. As the concentration of $CdCl_2$ decreases the potential slightly changes and becomes more negative (the scale of the figures is such that this displacement is almost imperceptible). For calculations, the conventional standard potential was taken as $E^*(Cd^{2+}/Cd) = -1.499$ V against Cl_2/Cl^- at 773 K, calculated from data reported in Ref. [29]. The initially observed potential corresponds to the equilibrium potential of cadmium, but then gradually shifts to a region of more positive values. According to the data [2] at 773 K and concentration $[UCl_3] = 0.049$ mol.% the conventional standard potential $E^*(U^{3+}/UN) = -1.944 \pm 0.1$ V vs. Cl_2/Cl^-. In our experiment 1.4 (Fig. 2) the maximum UCl_3 concentration was $[UCl_3] = 0.25$ mol.%. Then the equilibrium potential is $E(U^{3+}/UN) = -1.91 \pm 0.1$ V. It is clear that the potential observed in our experiments does not correspond to the UCl_3/UN equilibrium. According to paper [30] the conventional standard potential $E^*(U^{4+}/U^{3+})$ is −1.448 V vs. Cl_2/Cl^- at 773 K. If we assume that in our experiment the concentration of UCl_4 increases and becomes comparable to the concentration of UCl_3, the redox potential of the melt will be close to that observed. However, in our melt, in the presence of metallic cadmium, it is difficult to expect even small amounts of UCl_4 to appear. The $CdCl_2$/Cd electrochemical couple is evidently a buffer couple for stabilization of the redox potential of the system. Nevertheless, the potential of the medium after approximately 1200 min of experiment 1.4 (Fig. 3) and after ~500 min of experiment 1.6 (Fig. 8) becomes more positive than the potential of the $CdCl_2$/Cd couple. This may be explained by screening cadmium droplets at the bottom of the crucible with the black deposit of uranium nitride phases. It is clearly seen in Fig. 4a, d. As a result, metallic cadmium is excluded from the equilibrium. The potential of the melt is likely to be determined by electrode processes at the boundary of uranium nitride phases with the melt under investigation. Perhaps the potential of the melt is determined by the U_2N_3/U^{3+} or UN_2/U^{3+} couples, since it is known that U_2N_3 and UN_2 are semiconductors at 773 K [31,32]. To verify this assumption, at the end of some experiments we immersed the crucible with metallic cadmium into the melt. Metallic cadmium is supposed to reduce U^{4+}. The melt potential returned to the values close to the Cd^{2+}/Cd equilibrium potential for ~ 3–4 h.

In all experiments on the UN + $CdCl_2$ interaction at 773 K, at the bottom of the container with UN and at the bottom of the crucible, we found a black precipitate. According to the X-ray phase analysis, it consisted of different combinations of the UNCl, U_2N_3, U_4N_7, UN_2 phases, and also LiCl, KCl, K_4CdCl_6, UO_2 ones. The X-ray patterns

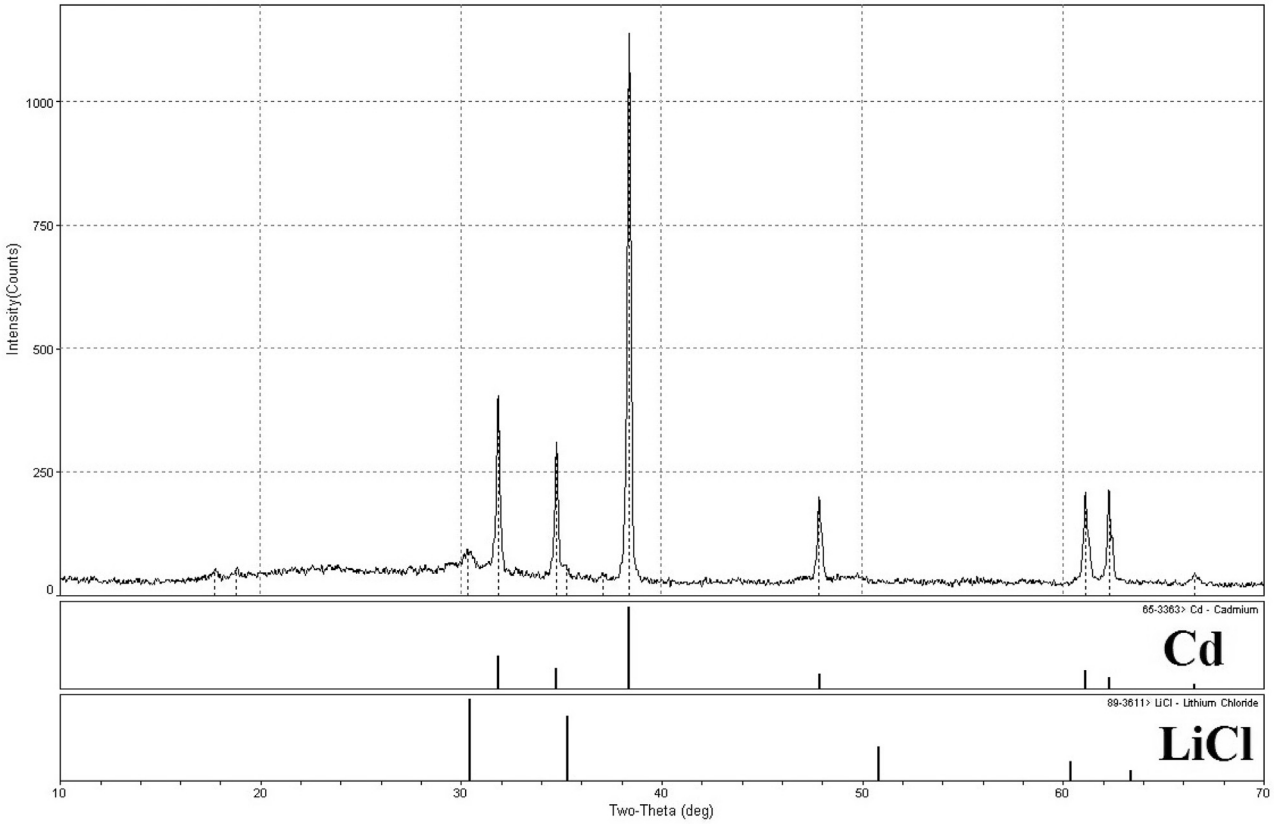

Fig. 7. X-ray diffraction pattern of sublimates in Exp. 1.4.

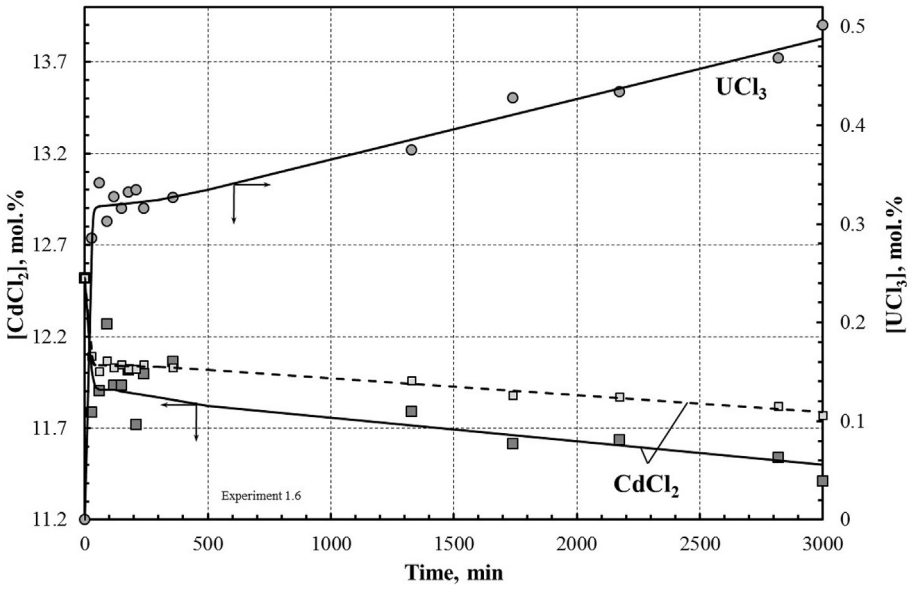

Fig. 8. $CdCl_2$ and UCl_3 concentration time dependences in Exp. 1.6. For $CdCl_2$ a solid line denotes the experimental data, a dotted line is the theoretical curve. Initial masses: m(UN) = 1.83 g; $m(CdCl_2)$ = 19.8 g; m(LiCl-KCl) = 42.1 g $[CdCl_2]_{init.}$ = 32.0 wt% = 12.5 mol.%. Initial molar ratio $CdCl_2$/UN = 14.9.

showed only a part of the listed phases, but at the same time, there were peaks that were not attributed to any compounds. They may correspond to the unknown phases or solutions of phases with shifted peaks. The original UN was not found in the samples. Apparently, it was completely consumed during the reaction. A small amount of UO_2 was found in the deposits, due to its presence in the initial UN. A tendency that the increase in the $CdCl_2$/UN molar ratio results in the decrease in the total amount of deposits, was defined.

The sublimates in the upper cold part of the quartz test tube

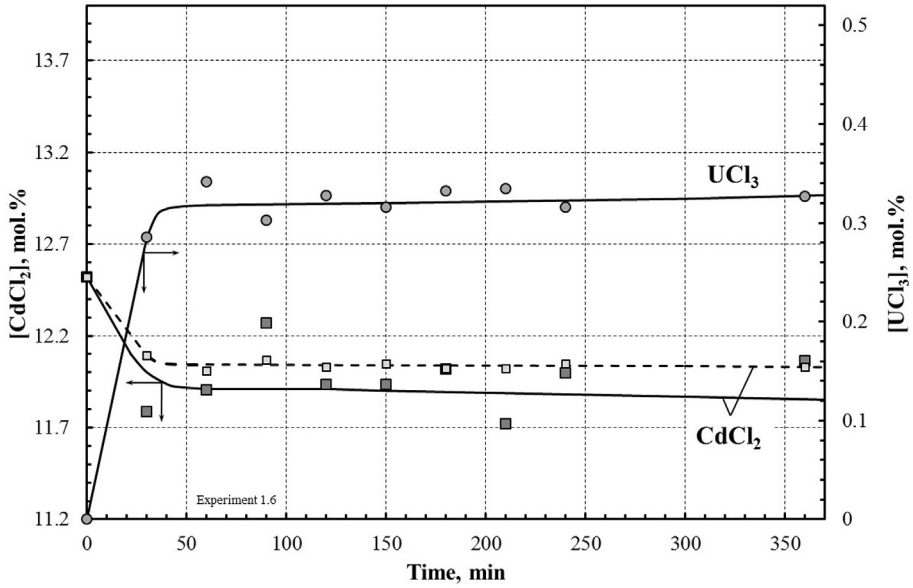

Fig. 9. Initial range of Fig. 8.

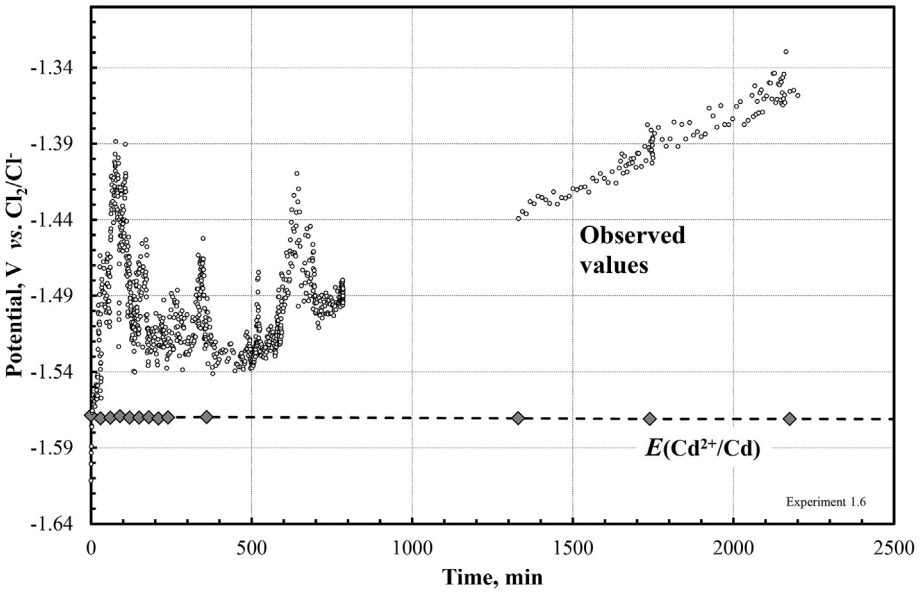

Fig. 10. Time dependence of the potential of molybdenum container with UN in Exp. 1.6. Sharp peaks correspond to sampling. A dashed line denotes the calculated equilibrium potential of cadmium in the melt.

formed in all experiments. They appeared after several minutes of the UN immersion into the melt and became more and more dense and opaque in the course of experiment. The color of the sublimates was gray, slightly brownish with metallic luster.

Metallic cadmium was found to form according to reaction (1) and possible reactions (3)–(7). Its melting point is equal to $T_m(Cd) = 594$ K and at 773 K its vapor pressure reaches 13.5 mm Hg [23]. This pressure is sufficient to vaporize partially metallic cadmium and entrain small amounts of salts. This process was also facilitated by nitrogen evolution. In different experiments, the mass of sublimates ranged approximately from 0.7 to 0.9 g. They predominantly consisted of metallic cadmium (70–90%). The $CdCl_2$ content was 4–14 wt % and the uranium content was 0.05–0.2 wt %. The LiCl and KCl mixture presented in the rest of the sample.

5. Conclusions

It is established that at 773 K the interaction between UN and $CdCl_2$ in the molten eutectic LiCl-KCl proceeds in two stages in a series of parallel reactions. The gross reaction can be divided into a fast one and a slow one. After termination of the fast stage, the $CdCl_2$ and UCl_3 concentrations change slowly, and the original UN is no longer detected among the reaction products.

The UNCl, U_2N_3, U_4N_7, UN_2 phases were revealed in the solidified salt by the X-ray phase analysis. The phases, apparently, were formed by parallel reactions during the first stage. A small amount of the UO_2 phase appeared due to the presence of oxygen in initial UN. The LiCl, KCl, K_4CdCl_6 phases formed at cooling of the melt.

As the value of mole ratio of $CdCl_2$/UN increased from 1.22 to

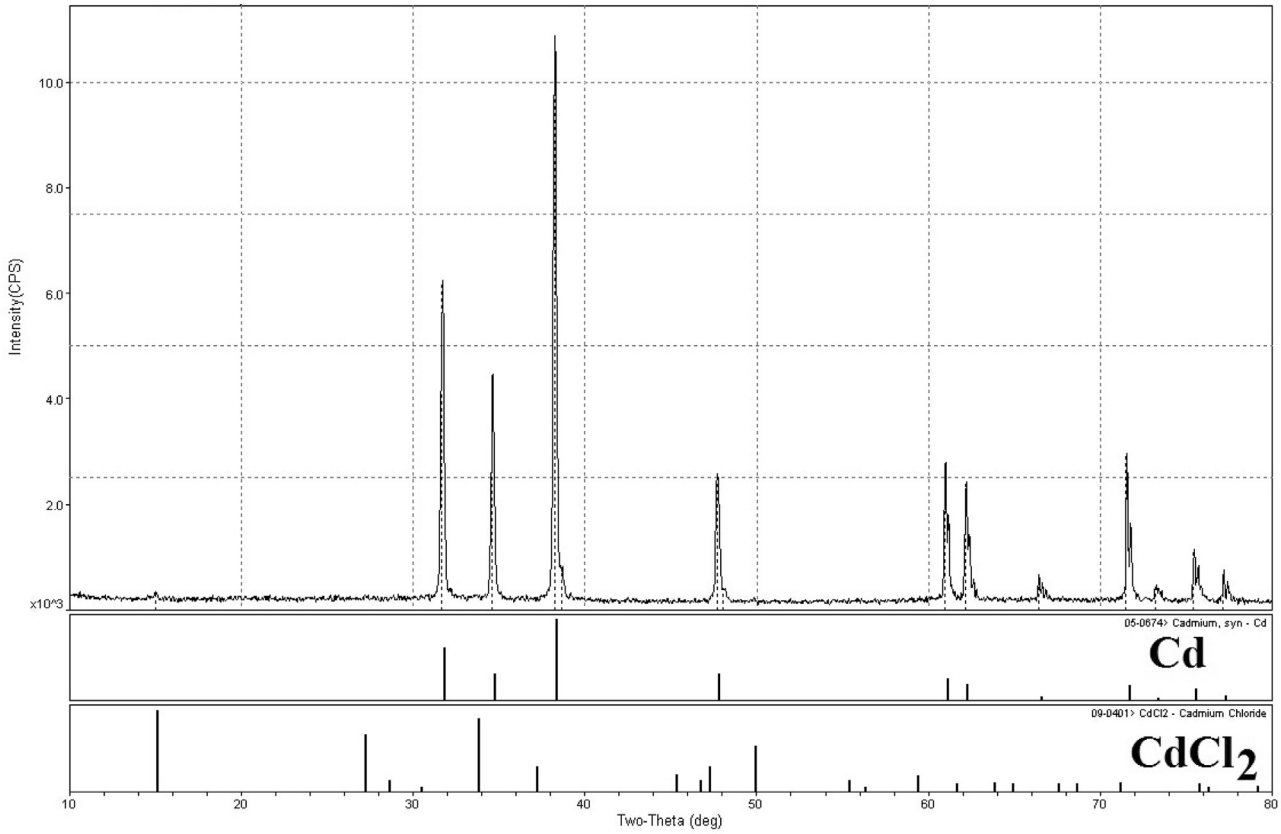

Fig. 11. X-ray diffraction pattern of sublimates in Exp. 1.6.

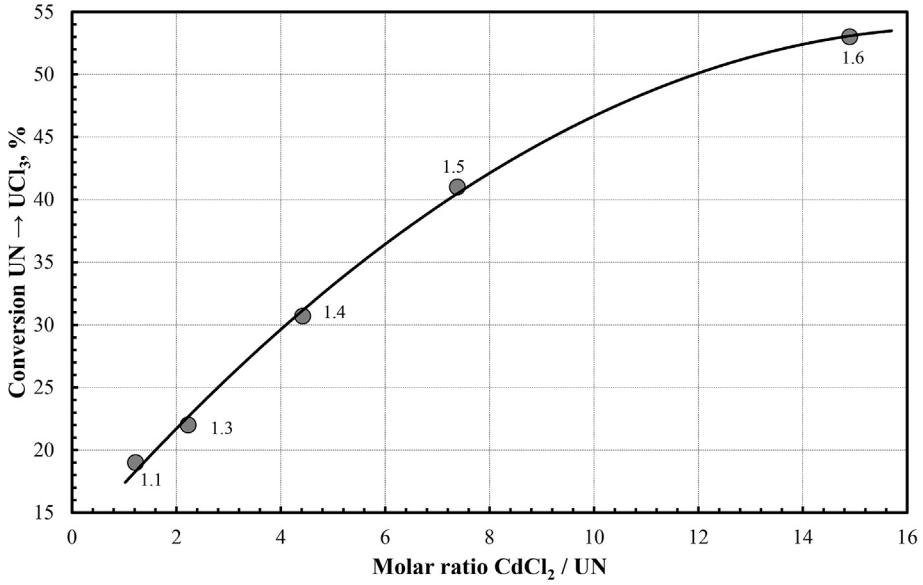

Fig. 12. Dependence of the UN → UCl_3 conversion *vs.* $CdCl_2$/UN molar ratio at 773 K. The numbers near the points are the numbers of the experiments. The initial masses of the UN tablets were as follows: exp. 1.1–3.038 g, exp. 1.3–1.85 g, exp. 1.4–1.87 g, exp. 1.5–1.12 g, exp. 1.6–1.83 g.

14.9, the fast reaction stage duration decreased from approximately 18 to 1 h, and the degree of conversion of UN → UCl_3 increased from about 19 to 53%. The experimental results achieved allow concluding that further research of the process conditions is necessary before the implementation of the "soft chlorination" technology.

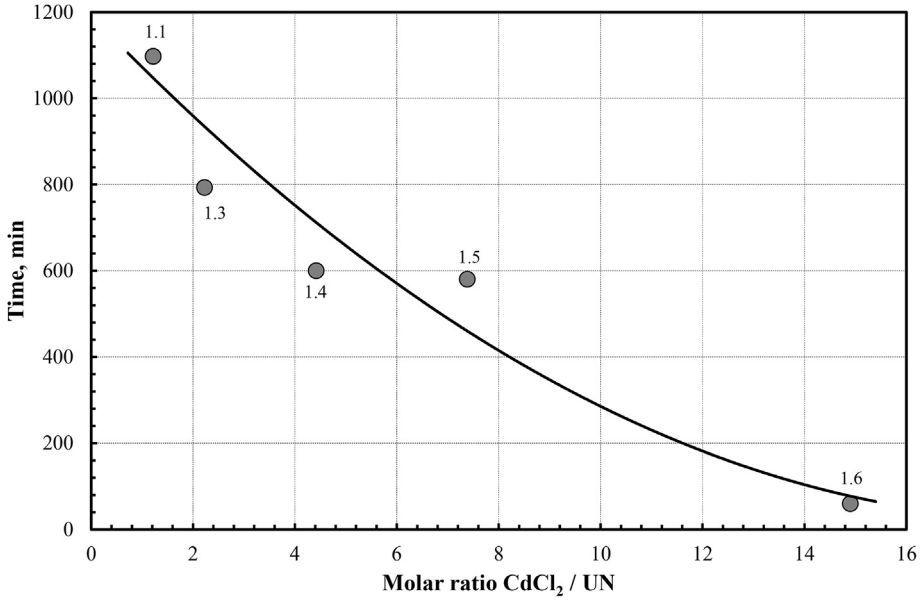

Fig. 13. Termination time of the fast reaction stage *vs* the mole ratio $CdCl_2$/UN at 773 K. The numbers near the points are the numbers of the experiments.

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